MECHANISMS OF STEAM GASIFICATION AND THE ROLE OF HYDROGEN INHIBITION
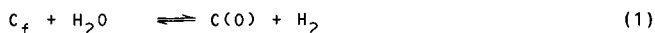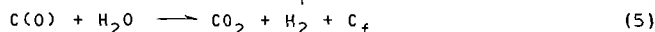
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ABSTRACT

Mechanism(s) of the carbon/steam reaction as published in literature are critically discussed. For this purpose, the various surface reactions are divided into primary and secondary reactions. Primary reactions involve a free active site:

$$C_f + H_2O \rightleftharpoons C(O) + H_2 \qquad (1)$$

$$C_f + H_2 \rightleftharpoons C(H_2) \qquad (2)$$

$$C_f + 1/2\ H_2 \rightleftharpoons C(H) \qquad (3)$$

Secondary reactions are consecutive reactions of the intermediate surface complexes:

$$C(O) \longrightarrow CO + C_f \qquad (4)$$

$$C(O) + H_2O \longrightarrow CO_2 + H_2 + C_f \qquad (5)$$

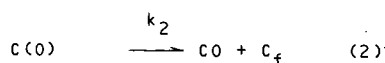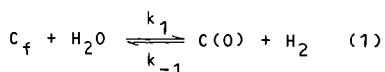$$C(H_2) + H_2 \longrightarrow CH_4 + C_f \qquad (6)$$

The probability of each reaction is examined in view of recent results in literature and own experimental observations, mainly based on TPD studies. Hydrogen inhibition reactions (1) to (3) are specially treated. The rate laws derived from eqs.(1) to (6) are tested by experimental studies. Hydrogen inhibition mainly results from reaction (3) and additionally from reaction (1).
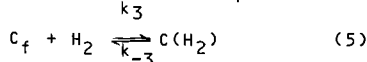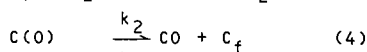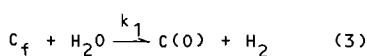
INTRODUCTION

The mechanism(s) and kinetics of the carbon/steam reaction are not yet fully understood (1-3), and this conclusion also holds for the strongly inhibiting effect of hydrogen as one of the reaction products (3-6).

The oldest and the most often used mechanisms for describing the carbon/steam reaction are the oxygen exchange mechanism A and the hydrogen inhibition mechanism B (1-3).

Mechanism A

$$C_f + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C(O) + H_2 \qquad (1)$$

$$C(O) \overset{k_2}{\longrightarrow} CO + C_f \qquad (2)$$

Mechanism B

$$C_f + H_2O \overset{k_1}{\longrightarrow} C(O) + H_2 \qquad (3)$$

$$C(O) \overset{k_2}{\longrightarrow} CO + C_f \qquad (4)$$

$$C_f + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C(H_2) \qquad (5)$$

In mechanism A the hydrogen inhibition results from the equilibrium of reaction (1), in mechanism B from the equilibrium adsorption of hydrogen according to eq. (5). Both mechanisms yield formally equal surface reaction rate r_S.

Mechanism A

$$r_S = \frac{c \cdot k_1 \cdot P_{H_2O}}{1 + \frac{k_1}{k_2} \cdot P_{H_2O} + \frac{k_{-1}}{k_2} P_{H_2}} \qquad (6)$$

Mechanism B

$$r_S = \frac{c \cdot k_1 \cdot P_{H_2O}}{1 + \frac{k_1}{k_2} \cdot P_{H_2O} + \frac{k_3}{k_{-3}} \cdot P_{H_2}} \qquad (7)$$

Only GIBERSON and WALKER (5) reported already in 1966 that the hydrogen inhibition is caused by dissociative chemisorption of hydrogen. In this case, eq.(5) of mechanism B has to be changed as follows:

$$C_f + \frac{1}{2} H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C(H) \qquad (8)$$

Eqs. (3), (4) and (8) lead to mechanism C. The resulting surface reaction rate is:

$$r_S = \frac{c \cdot k_1 \cdot P_{H_2O}}{1 + \frac{k_1}{k_2} \cdot P_{H_2O} + \frac{k_3}{k_{-3}} \cdot P_{H_2}^{0.5}} \qquad (9)$$

Mechanism C has recently been confirmed by YANG and YANG (6). The difference between mechanisms A or B and mechanism C is very important, because the inhibiting effect at low hydrogen partial pressures is much stronger if hydrogen is chemisorbed by dissociation.

All three mechanisms A, B and C have the same disadvantage. They are only applicable to the water gas reaction:

$$C + H_2O \rightleftharpoons CO + H_2 \quad , \qquad (10)$$
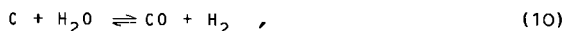
whereas steam gasification of carbon is a complex reaction which includes at least two consecutive reactions, namely the carbon monoxide shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad , \qquad (11)$$

and the methane formation by methanation of carbon monoxide

$$CO + 3 H_2 \rightleftharpoons CH_4 + H_2O \quad , \qquad (12)$$

or the methane formation by hydrogasification

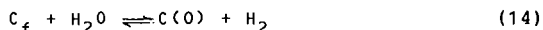$$C + 2 H_2 \rightleftharpoons CH_4 \quad . \qquad (13)$$

Modern gasification technologies use total pressures of at least

2 MPa, which favours the consecutive reactions. For such conditions, rate equations have been proposed for instance by BLACKWOOD (7) and MÜHLEN (8). Both authors use the adsorption term of mechanism A or B.
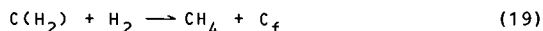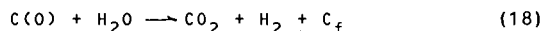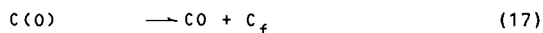
The present paper is concerned with an analysis of the probable mechanism(s) of the carbon/steam reaction with special consideration of the hydrogen inhibition. The analysis is based on informations given in literature and own experimental results.
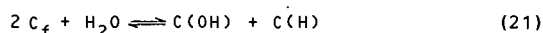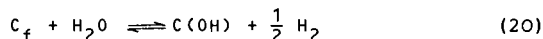
ANALYSIS OF THE CARBON/STEAM REACTION

The surface reactions in the carbon/steam reaction may be devided into primary and secondary reactions. <u>Primary reactions</u> are such ones in which a free active site is involved:
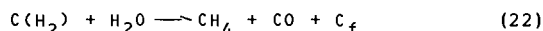
$$C_f + H_2O \rightleftharpoons C(O) + H_2 \qquad (14)$$

$$C_f + H_2 \rightleftharpoons C(H_2) \qquad (15)$$

$$C_f + \frac{1}{2} H_2 \rightleftharpoons C(H) \qquad (16)$$

<u>Secondary or consecutive reactions</u> are thus reactions of the intermediate carbon surface complexes:

$$C(O) \longrightarrow CO + C_f \qquad (17)$$

$$C(O) + H_2O \longrightarrow CO_2 + H_2 + C_f \qquad (18)$$

$$C(H_2) + H_2 \longrightarrow CH_4 + C_f \qquad (19)$$

Many further surface reactions may be assumed, for instance instead of eq.(14):

$$C_f + H_2O \rightleftharpoons C(OH) + \frac{1}{2} H_2 \qquad (20)$$

$$2 C_f + H_2O \rightleftharpoons C(OH) + C(H) \qquad (21)$$

or instead of eq.(19)

$$C(H_2) + H_2O \longrightarrow CH_4 + CO + C_f \qquad (22)$$

In the following the eqs.(14) to (19) will be examined only. At a first view they seem to be the most probable ones. The experimental results show that some of these are probably less whereas other ones are more important.

Eq.(14) is the decisive primary reaction. It is assumed to be an equilibrium reaction. This is in accordance with mechanism A. C(O) surface complexes may easily be reduced by hydrogen. In gasification with H_2O/H_2 mixtures their concentration depends on the H_2O to H_2 ratio. Both conclusions result from extensive TPD measurements, whereby carbon monoxide desorption was measured after quenching the samples from gasification to room temperature (9,10). YANG and YANG (6) also assume that eq.(14) is an equilibrium reaction but they do not consider this conclusion in deriving the rate equation.

The non-dissociative and dissociative chemisorption of hydrogen according to the eqs.(15) and (16) are parallel reactions of eq.(14). Both sorption mechanisms are discussed in literature (mechanisms B and C). Hydrogen desorption from the $C(H_2)$ complex, i.e. from aliphatically bound hydrogen, occurs at about 600 ^{O}C. Hydrogen desorption from the C(H) complex or of aromatically bound hydrogen requires temperatures above 800 ^{O}C (9,10). TPD measurements show hydrogen desorption at about 600 ^{O}C only in the case of low temperature chars after gasification in H_2O/H_2 mixtures. High temperature chars or carbons desorb hydrogen nearly exclusively above 800 ^{O}C, even if the gasification is performed with H_2O/H_2 mixtures. With such carbons methane formation is small. $C(H_2)$ complexes are assumed to be the decisive intermediates in methane formation (11). If methane formation is negligible, the rate of eq.(15) must be zero (equilibrium). This is the case for eq.(16) under all conditions.

In summarizing eqs.(14) to (16) hydrogen may inhibit the gasification reaction in different ways and to different extents. According to the TPD measurements eq.(15) should be of less importance. Strongest inhibition doubtless results from dissociative chemisorption(eq.(16)). because the majority of carbon edge atoms is saturated by aromatically bound hydrogen (10). Hydrogen inhibition by dissociative chemisorption also follows from the results of kinetic studies by GIBERSON and WALKER (5) and YANG and YANG (6), which are very convincing. This conclusion leads to the question whether the equilibrium of eq.(14) has to be considered additionally. One case may be gasification at high hydrogen partial pressures.

The secondary reactions are based on the reactions of the C(O) surface complex and the $C(H_2)$ surface complex. The dissociation of the C(O) surface complex (eq.(17)) obviously is irreversible as assumed in all mechanisms. The reaction of the C(O) complex with steam (eq.(18)) is a competition reaction to the direct desorption of the C(O) surface complex. If the desorption of the C(O) complex represents the rate limiting step of gasification, which is assumed by most authors, the carbon dioxide formation according to eq.(18) represents an important reserve for increasing the gasification rate. High steam partial pressures favour carbon dioxide formation. The stability of the C(O) complex represents the decisive point. Stability increases with increasing heat treatment temperature of the char. Therefore, carbon dioxide yields increase with increasing heat treatment temperature of the char.

The reaction of the $C(H_2)$ surface complex with hydrogen is the decisive methane formation in hydrogasification (11), possibly also in steam gasification at high hydrogen partial pressures. At high steam partial pressures and small hydrogen partial pressures, methane formation according to eq.(22) is more probable. This conclusion leads to the question whether eq.(15) is important under these conditions.

Nevertheless, for a first approach eqs.(14) to (19) seem to be a useful basis for deriving rate equations of carbon gasification with steam, which have to be examined by experimental studies.

MECHANISMS AND KINETICS

For formulating mechanisms, the sequence of eqs.(14) to (19) will be changed. The following sequence is used:

Eq.(14): eq.(1), eq.(17): eq.(2), eq.(15): eq.(3), eq.(16): eq.(4), eq.(18): eq.(5), eq.(19): eq.(6). This rearrangement of equations is useful for an improved clarity of the mechanisms and kinetic equations.

For the water gas reaction, the new eqs.(1) to (4) have to be considered. The rates of eqs.(3) and (4) are zero (equilibrium adsorption). This assumption leads to the following rate equation:

$$r_S = \frac{c \cdot k_1 \cdot P_{H_2O}}{1 + \frac{k_1}{k_2} P_{H_2O} + \frac{k_{-1}}{k_2} P_{H_2} + \left[1 + \frac{k_{-1}}{k_2} P_{H_2}\right]\left[\frac{k_3}{k_{-3}} P_{H_2} + \frac{k_4}{k_{-4}} P_{H_2}^{0.5}\right]} \tag{23}$$

At low hydrogen partial pressures some terms may be neglected, whereby the rate equation of mechanism C is finally resulting.(eq.(9)). This equation is confirmed by the works of GIBERSON and WALKER (5) and YANG and YANG (6). The equilibrium constant of dissociative hydrogen chemisorption at graphite edge atoms was determined by YANG and YANG (6):

$$K_4 = \frac{k_4}{k_{-4}} = 2 \cdot 10^{-3} \cdot \exp(21650/RT), bar^{-0.5} \tag{24}$$

Eq. (24) yields remarkably high values, at 800 °C: 53, at 1000 °C: 10.

In the case of remarkable carbon dioxide formation the set of surface reactions has to be extended by the new eq.(5). The resulting rate equation is:

$$r_S = \frac{c \cdot k_1 \cdot P_{H_2O} \cdot \left[1 + \frac{k_5}{k_2} \cdot P_{H_2O}\right]}{1 + \frac{k_1 + k_5}{k_2} P_{H_2O} + \frac{k_{-1}}{k_2} P_{H_2} + \left[1 + \frac{k_5}{k_2} P_{H_2O} + \frac{k_{-1}}{k_2} P_{H_2}\right]\left[\frac{k_3}{k_{-3}} P_{H_2} + \frac{k_4}{k_{-4}} P_{H_2}^{0,5}\right]} \tag{25}$$

This equation may also be simplified. As far as the steam conversion and thus the partial pressure of hydrogen are small, the following equation may be used:

$$r_S = \frac{c \cdot k_1 \cdot P_{H_2O} \left[1 + \frac{k_5}{k_2} \cdot P_{H_2O}\right]}{1 + \frac{k_1 + k_5}{k_2} P_{H_2O} + \left[1 + \frac{k_5}{k_2} P_{H_2O}\right] \frac{k_4}{k_{-4}} P_{H_2}^{0.5}} \tag{26}$$

Experimental results at steam partial pressures up to 0.8 MPa could

well be described by eq. (26). However, an improved fit was obtained by neglecting the term $(k_2+k_5) \cdot P_{H_2O} \cdot k_2^{-1}$. This means that the dissociative chemisorption of hydrogen may represent the dominating, inhibiting process.

The rate equation of the water gas reaction with simultaneous formation of methane may be derived by using the new eqs. (1) to (4) plus eq. (6). The rate equation is as follows:

$$r_s = \frac{c \left[k_1 \cdot P_{H_2O} \cdot c_2 + \frac{k_3}{k_{-3}} \cdot k_5 \cdot P_{H_2}^2 \cdot c_1 \right]}{\frac{k_1}{k_2} \cdot P_{H_2O} \cdot c_2 + \frac{k_3}{k_{-3}} \cdot P_{H_2} \cdot c_1 + \left[1 + \frac{k_4}{k_{-4}} P_{H_2}^{0.5} \right] \cdot c_1 \cdot c_2} \tag{27}$$

$$c_1 = 1 + \frac{k_{-1}}{k_2} P_{H_2} \; ; \qquad c_2 = 1 + \frac{k_5}{k_{-3}} P_{H_2}$$

An experimental test of eq. (27) is extremely difficult because 8 constants have to be determined. A more promising way to prove eq. (27) would be an examination of pure hydrogasification. As follows from the general discussion of the single steps of gasification it is obvious that this gasification is also inhibited by dissociative chemisorption of hydrogen.

RESULTS AND DISCUSSION

The detailed results of experimental studies are given in another paper [12]. For determination of the rate constants the initial reaction rates were used. They are obtained by plotting the gas formation or gasification rates versus the degree of carbon conversion X at X = 0. Initial reaction rates are independent of any changes of porosity, internal surface area or particle size.

The experimental results show that the dissociative chemisorption of hydrogen plays a dominating role in steam gasification and it probably represents the main inhibiting effect. From the present results it can not yet be decided whether the equilibrium of the dissociation reaction of steam according to eq. (1) has an additional inhibiting effect or not. This question is investigated in recent studies. In any case, it may be concluded that the non-dissociative chemisorption of hydrogen plays no role and it may therefore be neglected.

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